CARBOXYMETHYL CELLULOSE AS THE BINDER FOR THE LITHIUM-SULFUR BATTERIES

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Abstract: Demand for the high energy density batteries significantly increased along with the rapid development of new power source depending technologies. While these technologies are rapidly evolving, the battery industry is lagging behind unable to meet the demand. As a prospective successor to the existing li-ion battery technology, can be the high-capacity lithium-sulfur battery system (Li-S). The most commonly used composition of the positive electrode material of Li-S batteries is a mixture of sulfur, carbon and PVDF[1] binder mixed in NMP[2] solvent, which is (according to the WHO[3]) slightly toxic. The article deals with a replacing PVDF with organic non-toxic water-soluble binder.

Keywords: Accumulator, Battery, Binders, Cathode, Li-S, Lithium, Organic, Sulfur, Water-soluble

1 INTRODUCTION

Worldwide demand for energy sources has increased over the last decade, mainly thanks to the rapid growth of wearable devices and electrical vehicles. Existing li-ion battery technology is approaching to its technical limits and ceases to be sufficient to meet this demand. Therefore, new battery technologies must overcome the limits of current li-ion technology. One of these technologies is the lithium-sulfur battery system (Li-S or LSB).

High-capacity lithium-sulfur batteries have the potential in the near future to replace li-ion batteries, which are close to their technical limits. Sulfur as the active material of the positive electrodes is a particularly promising due to its high theoretical capacity of 1672 mAh/g, high availability and low cost (sulfur is one of the abundant elements).

However, lithium-sulfur battery system has some problems, that have to be resolved before it could be successfully deployed into commercial production. The commercialization of this technology is hindered by significant capacity fading problem, which is caused by irreversible oxidation of sulfur active material during the cycling of the cell.

2 LITHIUM-SULFUR ACCUMULATOR

Lithium-sulfur cells are composed of metallic lithium on the side of negative electrode and sulfur-containing cathode material deposited on aluminum current collector on the side of positive electrode. Since sulfur has weak conductivity $1x10^{-15}$ S/m, the cathode material must contain a conducting element (most commonly carbon) and therefore also binder (most commonly PVDF). The most commonly used electrolyte is composed of LiTFSI:$LiNO_3$[4] salts dissolved in DME:DOL[5] solvents.

[1] PVDF – Polyvinylidene fluoride
[2] NMP – N-methyl-2-pyrrolidone
[3] WHO – World Health Organization
[4] LITFSI - Lithium bis(trifluoromethanesulfonyl)imide, $LiNO_3$ - Lithium nitrate
[5] DME - 1,2-dimethoxyethane, DOL - 1,3-dioxolane

Unlike lithium-ion batteries, which are working on the principle of the intercalation process, the lithium-sulfur battery is the conversion type of the battery, and its discharging and charging involve electrochemical reactions.

The negative electrode reaction:

$$2Li \leftrightarrow 2Li^{+} + 2e^{-} \quad (1)$$

The positive electrode reaction:

$$S + 2e^{-} \leftrightarrow S^{2-} \quad (2)$$

The overall reaction (→ discharging, ← charging):

$$2Li + S \leftrightarrow Li_2S \quad (3)$$

Sulfur has the great variety of molecular forms; therefore, the allotropy of sulfur is complex. The most wide-spread and most stable allotrope of sulfur in nature is the orthorhombic α-form S_8 molecule (cyclo-octasulfur) in the shape of a ring or "crown". The α-form S_8 has a density of 2.069 g/cm^3 and is a great electrical insulator. Because of the usage of α-form S_8, the actual overall reaction, could be described as: [1]

$$16Li + S_8 \leftrightarrow 8Li_2S \quad (4)$$

At the start of the discharge of the cell, ring sulfur molecules are opened and receive the lithium ions, which leads to creation of lithiated polysulfide chains Li_2S_8. Furthermore, discharging causes the chains to break down into smaller chains ending at Li_2S, when the cell is considered to be discharged. Some of these intermediate chains are soluble in the electrolyte and are settling on the surface of the negative lithium electrode, which results in so-called shuttle effect (or shuttle phenomenon). Polysulfides shuttle results in corrosion of lithium electrode and loss of active material of positive electrode, which will reflect in self-discharging of the cell and lower coulombic efficiency. Figure 1. shows briefly the electrochemical reactions occurring in the Li-S cell during the discharge. [2]

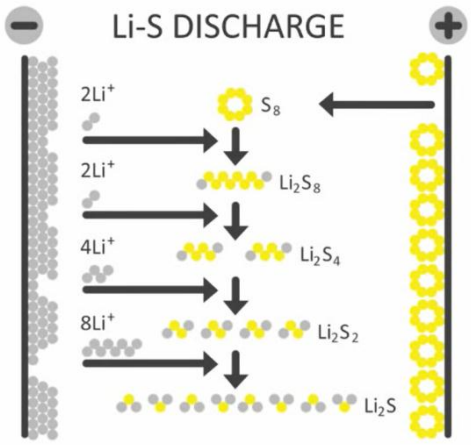

Figure 1: Brief description of electrochemical reactions occurring in a lithium-sulfur cell during its discharge. [3]

Another shortcoming of lithium-sulfur battery technology is a considerable volume change (circa 80%) during cycling of the cell, resulting from the fact that the final discharge product Li_2S has a different density (1.66 g/cm^3) than the initial α-form S_8. This volume change causes an internal stress on the electrode material resulting in its disintegration and loss of conductive contact between electrode material and current collector and electrode material itself. [2][4]

One of the areas of lithium-sulfur battery research is the research of binders capable of maintaining the cell's internal integrity during cycling while keeping the polysulfides in the vicinity of the positive electrode.

3 EXPERIMENTAL

Several samples of the electrodes have been made. As the reference electrode, an electrode composed of 60% Sulfur (Sigma Aldrich ≥99.5%) 30% Super P Carbon Black and 10% PVDF was made. Reference electrode's materials were dissolved in the NMP solvent and mixed in a magnetic stirrer for 24 hours. Since this preparation method has proved to be insufficient in the case of water-soluble carboxymethyl cellulose binder (CMC) and no uniform bonding of the materials was achieved, this electrode was prepared slightly differently and the second reference PVDF electrode was formed by the same preparation method. Materials were first mixed in a planetary ball mill for 15 minutes at 400 rpm and then poured with distilled water and again mixed on a magnetic stirrer. The same procedure was used for the second reference electrode containing PVDF binder to make results comparable. All the electrodes were then applied to the aluminum current collector by slurry coating method with 200 µm layer-thickness coating bar. The materials deposited on the current collectors were dried at 60°C for 24 hours and then circular electrodes of a 18mm diameter were cut off. All measured electrodes were pressed with a pressure of 300 kg/cm^2 and inserted in the argon glove box into the electrochemical measuring cells (El-Cell®). As a counter-electrode, the circular lithium metal was used and the 130 µl of electrolyte (LiTFSI/$LiNO_3$ in DME:DOL) were dropped in the cell.

In an attempt to monitor operating mechanisms of Li-S sample cells, several techniques have been used, including spectroscopic and electrochemical analyzes. Energy dispersive spectroscopy (EDS) in scanning electron microscope (SEM) was used to analyze the surface structure of the electrode samples and the distribution of the elements on their surfaces (before pressing).

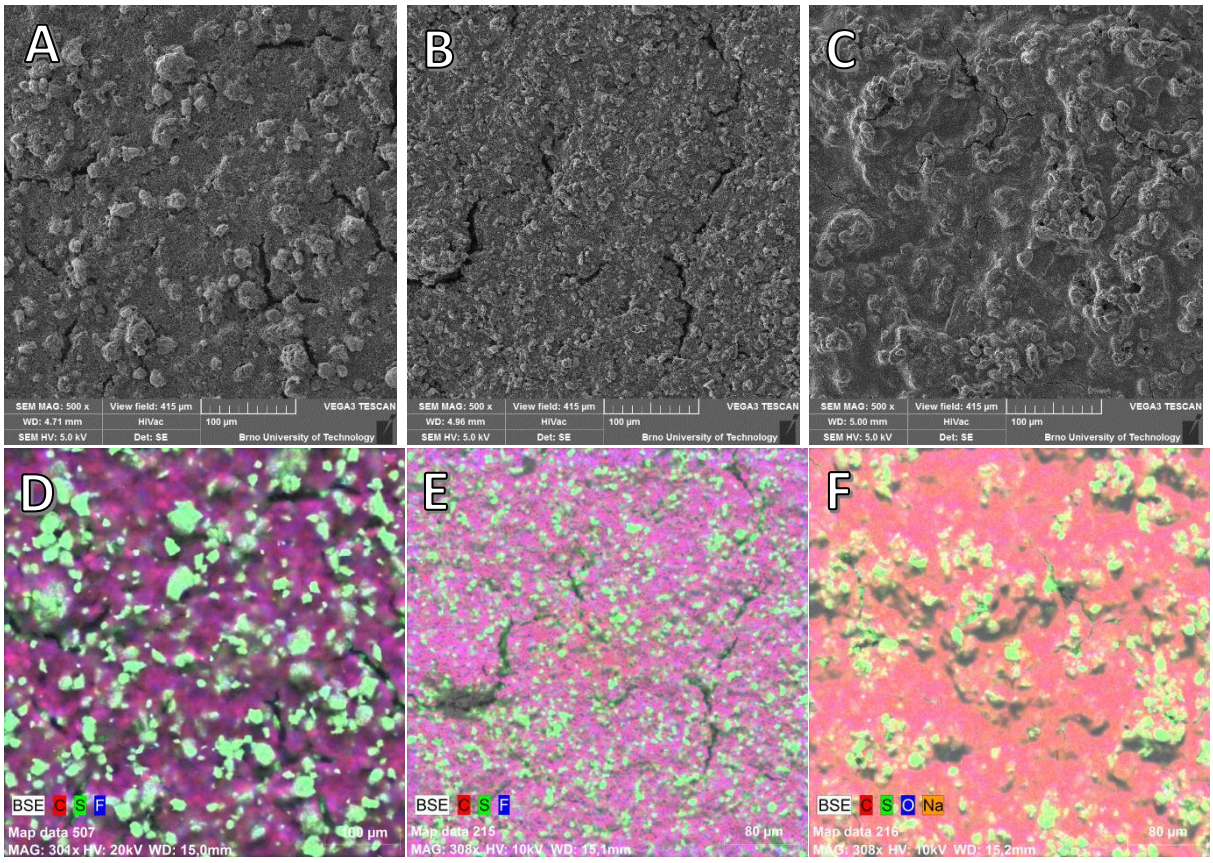

Figure 2: A) Surface structure of the 1st reference PVDF electrode
B) Surface structure of the 2nd reference PVDF electrode
C) Surface structure of CMC electrode
D) Elements distribution (C, S, F) of the 1st reference electrode
E) Elements distribution (C, S, F) of the 2nd reference electrode
F) Elements distribution (C, S, O, Na) of the CMC electrode

As can be seen from the surface structure and element distribution of sample electrodes (Figure 2.), there is already significant difference between reference electrodes created by different methods. On the surface of the 1st reference electrode, it is possible to notice larger sulfur clusters as on the 2nd reference electrode and the 1st electrode appears to be more porous. On the other hand, the CMC electrode looks completely closed and the distribution of sulfur clusters is not as even as in case of 1st and 2nd reference electrode. The non-porous structure of CMC electrode indicates excessive amount of binder and may lead to a decrease in the active material area.

For the electrochemical analysis two cycles of galvanostatic cycling with potential limitation (GCPL) at 0.1C were performed for all electrode samples assuming that the capacity of the active material is 1200 mAh/g. The capacity of the second discharge cycle was then used to recalculate the charging/discharging currents. After the recalculation, 20 cycles at 0.2C were performed (Figure 3.).

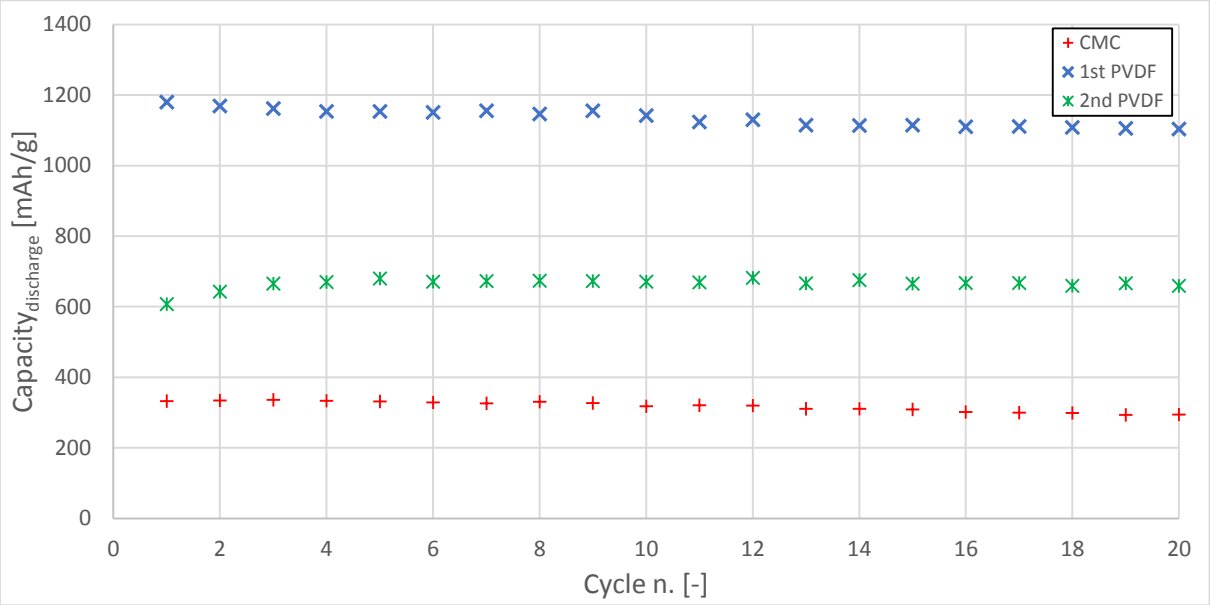

Figure 3: Comparison of galvanostatic cycling of the electrode samples (at 0,2C)

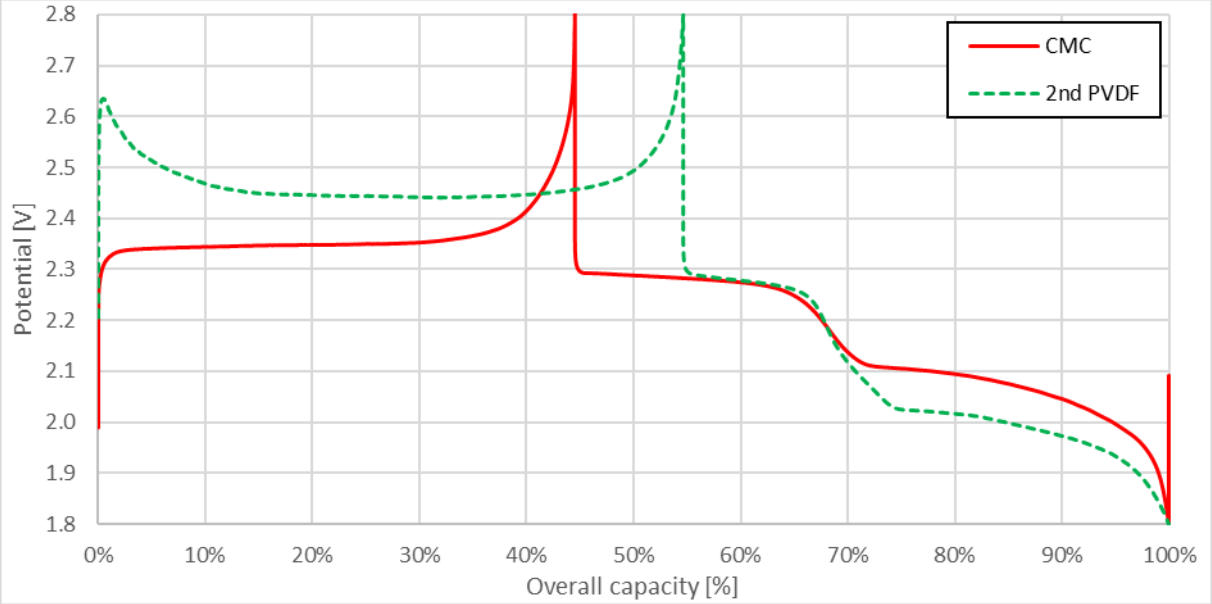

Figure 4: Comparison of first cycles of GCPL for CMC and 2nd PVDF electrodes

4 RESULTS AND DISCUSSION

As can be seen from the comparison of GCPL of the electrode samples, 1st PVDF electrode reaches almost twice the capacities as 2nd PVDF electrode and thrice the capacities as CMC electrode. This is most likely due to higher porosity and thus higher active area than in the case of remaining electrodes. Before GCPL at 0.2C, 2nd PVDF and CMC electrode were disconnected for 2 days due to maintenance of the measuring device, which is reflected in the first GCPL cycles. However, this disconnection has shown that the CMC electrode did not self-discharge for 2 days, as was the case with 2nd PVDF electrode. Comparison of the first GCPL cycles at 0.2C of these electrodes can be seen at Figure 4. This indicates that carboxymethyl cellulose binder may hold polysulfides in the positive electrode area.

5 CONCLUSION

From the research that has been done so far, it is clear that the carboxymethyl cellulose can be used as a binder for positive electrodes of Li-S batteries, however it is important to achieve a higher porosity of the resulting electrode in order to achieve higher capacities. To achieve greater porosity, the carboxymethyl cellulose binder content should be reduced. The measured results show that the use od a non-toxic organic and water-soluble binder in the production of positive electrodes of Li-S is possible and, moreover, this binder holds polysulfides in the positive electrode area.

ACKNOWLEDGEMENT

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